Exam Thermodynamics 2
03 November 2021

Please, hand in your answers to problems 1, 2, 3 and 4 on separate sheets.
Put your name and student number on each sheet.

The examination time is 12:45 until 15:45, so **three hours**.
There are 4 problems, with each 4 subproblems, a list of constants and a formulae sheet,
6 pages in total.
All 16 subproblems have equal weight for the final grade.

Problem 1

a) Give a definition **and** *short* description of the following concepts
-Equipartition theorem
-Henry constant
-Isopleth
-Critical nucleus
-Solubility

b) Give the characteristic equation for the Helmlholtz free energy for an open system with two components A and B and electric work; use it to find a Maxwell relation between the chemical potential of component B and the entropy.

c) Give the meaning of all symbols in the following formula as well as a description of its use in thermodynamic problems.

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^\ominus}$$

d) The mean activity coefficient of AgCl dissolved in water at $T = 298.15$ K is determined to be $\gamma_\pm = 0.900$, using the Debye-Hückel limiting law.
Use the Debye-Hückel limiting law to find the mean activity coefficient at $T = 275.00$ K of that solution with the same molality.

Problem 2

The excess volume of a mixture is defined as $V^E \equiv V - V_{ideal}$, in which V is the real volume and V_{ideal} is the volume of an ideal mixture, i.e. a mixture in which all molecules have the same interactions, no matter the type.

A mixture of two compounds (compound A and compound B) has a molar excess volume of $V_m^E = x_A x_B (a_0 + a_1(x_A - x_B))$ at a temperature T_0. $x_i = n_i/n$ represents the mole fraction of component i, $a_0 = -2.4697$ cm^3/mol and $a_1 = 0.0608$ cm^3/mol. The molar volumes of the pure compounds at T_0 are $V_{m,A} = 76.00$ cm^3/mol and $V_{m,B} = 77.00$ cm^3/mol.

a) Find an expression for the partial molar volumes of a binary *ideal* mixture in terms of the molar volumes.

b) Using the terms of the molar volumes, a_0, a_1, x_A and x_B at the temperature T_0, show that the partial molar volumes V_A and V_B of the compounds in the mixture are given by

$$V_A = V_{m,A} + a_0 x_B^2 + a_1 (3x_A - x_B) x_B^2, \quad \text{and}$$

$$V_B = V_{m,B} + a_0 x_A^2 + a_1 (x_A - 3x_B) x_A^2.$$

Hint: First rewrite $V^E = (n_A + n_B)V_m^E$ in terms of n_A and n_B.

c) Calculate the partial molar volumes of both components in an equimolar mixture, at T_0.

d) Calculate the mole fraction x_B, at T_0, for which the partial molar volumes of the two components in the solution are equal, for the case that we can neglect the (relatively small) value of a_1.

Problem 3

Currently there is quite some research going on in the field of energy storage. Heat for warming houses and industrial processes is the major form of energy consumption in the world. Therefore, it would be beneficial to use the solar heat for that, but that demands for storage during summer time and reuse of the stored heat during winter time.

A promising method for heat storage is to use the heat exchange during a phase transition between different hydration states of a salt. The general reaction for such a phase transition is

$$\text{SALT} \cdot n\text{H}_2\text{O}(s) \leftrightarrows \text{SALT} \cdot m\text{H}_2\text{O}(s) + (n - m)\,\text{H}_2\text{O}(g).$$
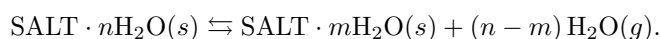
The released water vapour is collected and stored in a separate tank, and is reused for the reverse reaction.

A promising example is potassium carbonate, which has a stable hydrate $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$, the so-called sesquihydrate, and a stable anhydrate K_2CO_3, both depending on the conditions.

In the figure below the $(P_{\text{H}_2\text{O}} - T)$ phase diagram of the (s-g) system is given, where $P_{\text{H}_2\text{O}}$ is the partial pressure of the water vapour in the system.

a) Show that the equilibrium constant K of the reaction between the anhydrate K_2CO_3 and the sesquihydrate $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ only depends on the activity $a_{\text{H}_2\text{O}(g)}$ **and** determine K in terms of $a_{\text{H}_2\text{O}(g)}$.

b) Use the data in the phase diagram to determine the enthalpy change for the dehydration transition, so $\Delta H(\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O} \to \text{K}_2\text{CO}_3)$, **and** discuss what the direction of the reaction is when heat is stored in the salt.

Hint: assume that the water vapour can be treated as a perfect gas and that the enthalpy change is independent of the temperature, so we can use the van't Hoff equation

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$
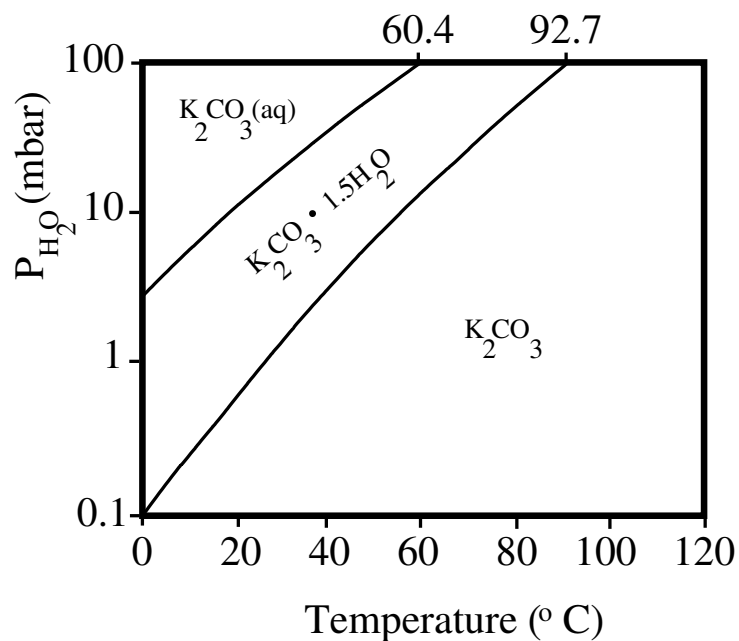
c) Use the result of the former part to find the entropy change for the dehydration transition at 20 °C.

d) Deliquescence is the process by which a substance absorbs water vapour from the atmosphere until it dissolves in the absorbed water and forms a solution. Deliquescence occurs when the partial pressure of water vapour in the environment is equal to (or larger than) than the equilibrium vapour pressure of the salt.

The relative humidity at temperature T is defined as the actual partial pressure of water vapour in the air as a fraction of the maximum (equilibrium) partial pressure of water vapour at that temperature:

$$RH = \frac{P_{H_2O}}{P_{H_2O}^{sat}} \times 100 \ \%$$

At 20 °C the vapour pressure of bulk water is 2.330 kPa.

Use the phase diagram to estimate the relative humidity for which deliquescence starts at 20 °C .

Problem 4

We study the spontaneous formation of clusters of molecules in an aqueous solution of the para-chlorobenzenesulphonate salt of the amino acid alanine (ALACBS; $M = 282$ g/mol) at 340 K. Such clusters are continuously formed and dissociated leading to an average size distribution which is temperature dependent.

We restrict our study to a saturated solution of the salt and assume that all clusters can be considered as having a spherical shape with an isotropic surface tension γ.

In 1990 Mersmann deduced a relation between the solubility c_l of a compound and the surface tension γ for the interface between the solid (in the present case the clusters) and the saturated solution, according to

$$\gamma = \frac{2}{(36\pi)^{1/3}} (c_s N_A)^{2/3} kT \ln \left[\frac{c_s}{c_l} \right].$$

In this expression c_s is the density of the compound in its solid phase, which in the present case is $c_s = 5.5 \cdot 10^3$ mol/m^3 and $c_l = 250$ mg/mL is the solubility of the salt. All other symbols have the usual meaning.

a) Calculate the surface tension γ for the saturated ALACBS solution, in J/m^2.

b) Calculate the pressure inside a spherical cluster, containing $n = 6$ ALACBS-molecules, under standard conditions.

c) Show that the work $W_c(n)$ for the formation of a cluster of n molecules in the solution is given by

$$W_c(n) = \left(\frac{9}{4\pi} \right)^{1/3} \gamma \left[\frac{n}{c_s N_A} \right]^{2/3}.$$

Hint: For a saturated solution there is no difference between the chemical potential of a molecule in solution and the chemical potential of a molecule in the (bulk) solid phase.

d) Let $C(n)$ be the average concentration of clusters having n ALACBS-molecules. Clusters having only a single ALACBS-molecule can be regarded as a dissolved molecule.

Use the Boltzmann distribution function to find an expression for the concentration ratio $\frac{C(n)}{C(1)}$ and determine its value for $n = 10$.

List of constants

Elementary charge	e	$1.602 \cdot 10^{-19}$ C
Faraday's constant	F	$9.648 \cdot 10^4$ Cmol^{-1}
Vacuum dielectric constant	ϵ_0	$8.854 \cdot 10^{-12}$ C^{2}J^{-1}m^{-1}
Boltzmann's constant	k	$1.381 \cdot 10^{-23}$ JK^{-1}
Planck's constant	h	$6.626 \cdot 10^{-34}$ Js
Bohr magneton	μ_B	$9.274 \cdot 10^{-24}$ JT^{-1}
Atomic mass constant	m_u	$1.661 \cdot 10^{-27}$ kg
Amadeo Avogadro di Quaregna e Ceretto's constant	N_A	$6.022 \cdot 10^{23}$ mol^{-1}
Gas constant	R	8.314 JK^{-1}mol^{-1}
Free fall acceleration	g	9.807 ms^{-2}
Unit of energy		1 cal = 4.184 J
Standard pressure	$P^\ominus$	1 bar = 10^5 Nm^{-2} = 0.9869 atm = 750 Torr

Formulae Thermodynamics (1)

$$PV = nRT = NkT$$

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT$$

$$\Delta U = W + Q$$

$$dW = -P_{ext.}dV + dW' \quad \text{and} \quad dW'_{max} = (dG)_{P,T}$$

$$dQ|_P = C_P dT \quad \text{and} \quad dQ|_V = C_V dT$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

$$dS = \frac{dQ^{rev}}{T} \geq \frac{dQ}{T}$$

$$dS_{tot} = dS + dS_{omg} \geq 0$$

$$dU = -PdV + TdS + \sum_i \mu_i dn_i$$

$$H = U + PV$$

$$dH = VdP + TdS + \sum_i \mu_i dn_i$$

$$A = U - TS$$

$$dA = -PdV - SdT + \sum_i \mu_i dn_i$$

$$G = H - TS$$

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta_r G^{\ominus} + RT \ln Q, \quad \text{where} \quad Q = \prod_i a_i^{\nu_i}$$

$$RT \ln K = -\Delta_r G^{\ominus}$$

$$E = E^{\ominus} - \frac{RT}{\nu F} \ln Q \quad \text{and} \quad dW' = Edq \quad \text{and} \quad E = IR \quad \text{and} \quad P = EI$$

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i = \mu_i^{\ominus} + RT \ln \frac{P_i}{P^{\ominus}}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j d\mu_j = 0$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\mathrm{trs}}H}\right) x_B$$

$$\Delta S = -nR \left(x_A \ln x_A + x_B \ln x_B\right)$$

$$\Pi = [B]RT = \frac{n_B}{V} RT$$

$$S = k \ln W$$

$$\frac{n_i}{N} = \frac{\exp \frac{-\epsilon_i}{kT}}{q}, \quad \text{where} \quad q = \sum_i \exp \frac{-\epsilon_i}{kT} \quad \text{and} \quad <X> = N<x> = N \sum_i x_i \frac{n_i}{N}$$

Formulae Thermodynamics 2

$$\left(\frac{\partial V}{\partial T}\right)_{P,W',n_i} = -\left(\frac{\partial S}{\partial P}\right)_{T,W',n_i}$$

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

$$P_j = x_j P_j^*$$

$$P_j = y_j P$$

$$P_B = x_B K_B$$

$$\left(\frac{\partial \mu_\beta}{\partial P}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T = \Delta_{\mathrm{trs}}V$$

$$\left(\frac{\partial \mu_\beta}{\partial T}\right)_P - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P = -\Delta_{\mathrm{trs}}S$$

$$P = P^* \exp\left(\frac{V_m \Delta P}{RT}\right)$$

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V} = \frac{\Delta_{\mathrm{trs}}H}{T\Delta_{\mathrm{trs}}V}$$

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} \approx \frac{\Delta_{\mathrm{trs}}H}{RT^2}$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\mathrm{trs}}H}\right) x_B \qquad \ln x_B = \frac{\Delta_{\mathrm{fus}}H}{R}\left[\frac{1}{T_{\mathrm{fus}}} - \frac{1}{T}\right]$$

$$\mu = \mu^\ominus + RT\ln a = \mu^\ominus + RT\ln x + RT\ln\gamma$$

$$\mu = \mu^\ominus + RT\ln a = \mu^\ominus + RT\ln\frac{b}{b^\ominus} + RT\ln\gamma$$

$$F = C - P + 2$$

$$n_\alpha l_\alpha = n_\beta l_\beta$$

$$\Delta_{\mathrm{solv}}G^\ominus = -\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i}\left(1 - \frac{1}{\epsilon_r}\right)$$

$$\gamma_\pm = \left(\gamma_+^p \gamma_-^q\right)^{\frac{1}{p+q}}$$

$$\log\gamma_\pm = -|z_+ z_-|A\sqrt{I}$$

$$I = \frac{1}{2}\sum_i z_i^2 \frac{b_i}{b^\ominus}$$

$$A = \frac{F^3}{4\pi N_A \ln 10}\left(\frac{\rho b^\ominus}{2\epsilon^3 R^3 T^3}\right)^{\frac{1}{2}}$$

$$P_{in} = P_{out} + \frac{2\gamma}{r} \qquad P = \rho g h \qquad w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \qquad \gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\Theta_c$$